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A Comparative Study of the Chemical
Behavior of
Pyrite and Marcasite.

THESIS PRESENTED TO THE FACULTY OF THE DEPARTMENT
OF PHILOSOPHY OF THE UNIVERSITY OF PENNSYLVANIA
FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY.

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While much has been done in the way of investigating the chemical properties and constitution of the various artificial chemical compounds, comparatively little attention has been paid to the constitution of the naturally occurring chemical compounds. The carbon compounds, for instance, have in an immense number of cases been investigated with sufficient exactness to allow of our expressing their constitution by means of structural formulæ, but to how many minerals, aside from the simplest compounds, can we assign structural formulæ that are based on any knowledge that we possess of their reactions? It is true that much has been done in the way of the artificial production of minerals, and some knowledge of the constitution of certain minerals has been arrived at by a study of their decomposition products, but very little in comparison to the extent of the field. There are probably several reasons for this neglect of the study of the chemical properties and constitution of minerals, as want of homogeneity in the minerals themselves, difficulty of procuring or separating pure material for investigation, and similar difficulties which do not so frequently occur with artificial compounds. It thus happens that mineral chemistry is not as much studied as it deserves to be. Certain groups of minerals have, however, received some attention; for instance, Prof. F. W. Clarke has been carrying on a very interesting series of investigations on the constitution of certain silicates which have been productive of most valuable results. The natural sulphides, sulpharsenides and sulpho-salts present some very interesting problems in regard to their constitution, and it was with a view of adding to our knowledge of the chemical behavior of two of these sulphides that I undertook the series of investigations about to be described.

The compound FeS_2 is found in nature in two well-known forms—the one Pyrite (the isometric mineral) and the other Marcasite (the orthorhombic mineral). Since the separation of the two names from the general term, pyrites, it has been recognized that the orthorhombic form is lighter in color and also of lower specific gravity than the isometric form. From early times, also, the greater tendency of “white pyrites,” or marcasite, to decompose in the air was well known.

Pyrite, the form which resists atmospheric weathering most thoroughly, is of a bright brass-yellow color and metallic lustre, breaking with an uneven conchoidal fracture, but bright on the surface of fracture. It crystallizes in the isometric system in forms showing generally pentagonal hemihedrism. Its specific gravity ranges from 4.8 to 5.2, averaging somewhat over 5. The brass-yellow crystals are generally quite unaltered in the air.

Marcasite, on the other hand, has a pale greenish or grayish yellow color, an uneven fracture, which shows a somewhat fibrous structure, and generally but little lustre on the surface of fracture. It crystallizes in the orthorhombic system, very commonly in twins or radiated fibrous masses. It is not very permanent in moist air, but readily decomposes and largely into FeSO_4 . The chemical formula of either form, calculated from quantitative analyses, is the same, FeS_2 or $\text{Fe} = 46.67\%$, $\text{S} = 53.33\%$.

The chemical study of these two minerals has been mainly confined to the formation of one of them artificially and to a few experiments on their relative decomposability. Pyrite has been made artificially in a number of ways; marcasite has not as yet been formed artificially.* In 1836, Wöhler† produced cubes and octahedra of pyrite by subjecting a mixture of ferric oxide, flowers of sulphur and ammonium chloride to a temperature a little above the volatilizing point of the ammonium chloride. The resulting mass was washed to isolate the crystals from the accompanying pulverulent matter. Stanislas Meunier‡ modified this method by mixing equal parts of ferrous carbonate and sulphur and heating in glass tubes over a moderate flame. When the excess of sulphur has been driven off, there remains a black powder containing a considerable percentage of cubes of pyrite. Dana§ states that pyrite may be made "by slow reduction of ferrous sulphate in presence of some carbonate." Baubigny|| produced FeS_2 as a crystalline crust by acting on metallic iron by a solution of SO_2 in water (H_2SO_3) in closed tubes and at a temperature of 200° . As neither this experiment nor the one immediately preceding it shows that the crystals were isometric, it is possible that both of them may be marcasite. Henri Saint Claire Deville¶ produced cubes of pyrite by melting a mixture of potassium sulphide (K_2S) and iron sulphide (FeS) in presence of excess of sulphur. This reaction, if correct as to the *cubical* product, is a remarkable one, as I should rather expect marcasite to result under such conditions. Senarmont** produced FeS_2 by decomposing a salt of iron by an alkaline sulphide at an elevated temperature in sealed glass tubes. The product was an amorphous black powder, not altering on exposure to air and not attacked by hydrochloric acid. This may have been pyrite, as marcasite is readily decomposed by moist air. Rammelsberg,†† in 1862, made FeS_2 pseudomorphs after ferric oxide (Fe_2O_3) by passing a current of hydrogen sulphide over it at a temperature between 100° and a red heat. The product of this reaction would likely be pyrite.

In nature it would seem that in most cases the sulphide of iron first

* Doelter, *Zeit. für Kryst.*, xi, 31, 1885; cf. Dana, *Syst. Min.*, 1892.

† *Pogg. Ann.*, xxxvii, p. 238.

‡ *Les Méthodes de Synthèse en Minéralogie*, S. Meunier, 1891.

§ J. D. Dana, *System of Mineralogy*, edition of 1868, p. 64.

|| S. Meunier, *Synth. Min.*, p. 279.

¶ Cited in *Dict. Chem.* of Wartz, by E. Wilm, article "Iron," T. i, p. 1414.

** S. Meunier, *Synth. Min.*, p. 285.

†† *Jour. für Praktische Chemie*, T. lxxxviii, p. 266.

formed is FeS , but probably by action of a ferric salt, or carbonic acid (H_2CO_3), causing a loss in iron FeS_2 results, and this is almost always pyrite. On the other hand, where ferrous sulphate has been reduced by slow action of decomposing organic matter, the resulting sulphide seems to be generally marcasite, which if not in crystals may be recognized by its ready weathering to ferrous sulphate (FeSO_4). This compound may, however, in many cases, be a mixture of pyrite and marcasite, as much pyrite seems to be.* These several ways in which pyrite may be formed are of importance as indicating the condition of the iron in the compound, and will be referred to later on.

Equally important as bearing on the constitution of these sulphides are the observations that have been made as to their decomposition under atmospheric agencies. On exposing crystallized pyrite to atmospheric weathering it is generally found that but little, if any, change takes place even in a year's time, while crystallized marcasite, under the same conditions, shows a rapid weathering. The main product of the weathering of pyrite in nature is the compound limonite, $\text{Fe}_4\text{O}_3(\text{OH})_6$, which occurs in large quantities in nature, evidently derived from pyrite. Its pseudomorphs after pyrite are very common. On the other hand, when marcasite weathers a very large percentage of ferrous sulphate (FeSO_4) is formed with a comparatively small percentage of limonite, unless the marcasite decomposes underground and under pressure, when limonite is largely produced.† Much of the excess of sulphur with marcasite is changed to sulphuric acid, but with pyrite much remains behind as sulphur. Some comparison of the rate of oxidation of these two minerals in the air is afforded by an examination of specimens in a collection. Here it will be found that most of the pyrite is unchanged, but nearly every specimen of marcasite will show tarnish if no other sign of oxidation, and often a considerable coating of oxide can be seen, or a white efflorescence of FeSO_4 .

Chemical investigations of these two minerals have been mainly in the way of analysis, but some experiments have been made in the way of studying their relative behavior towards certain reagents. Before describing my experiments, it will be necessary to briefly mention some of these.

Both minerals are decomposed by a solution of silver nitrate and gold chloride, the decomposition taking place quite rapidly.‡ My experiments in this connection are mentioned later.

A. A. Julien§ has shown that different samples of pyrite show a difference in their reaction with bromine vapor. His experiments consisted in exposing finely ground pyrite to the action of bromine vapor at the tem-

* Compare A. A. Julien, "Decomposition of Pyrite," *Ann. N. Y. Acad. Sci.*, Vols. iii and iv.

† Blum, *Pseudomorphosen*, 1843, pp. 197-199.

‡ S. Meunier, *Synth. Min.*, p. 309.

§ A. A. Julien, *Ann. N. Y. Acad. Sci.*, Vol. iv, pp. 151, 155.

perature of the air for twelve hours. The residue was extracted with dilute H_2SO_4 , which removed the iron rendered soluble (bromide), and the iron was then determined in this solution. The percentage of iron that had dissolved varied from 2.43 to 15.20 per cent., although all samples tested are described as pyrite. He also tried the action of bromine in aqueous solution, but the reaction was too rapid to give any comparative results.

Much more important are the results obtained in the oxidation of these minerals by the electric current as conducted by Prof. Edgar F. Smith,* and it was the remarkable results that were then obtained that induced me to continue the study of the comparative reactions of these two minerals. Smith found that a current which would completely oxidize the sulphur in marcasite in a given time would oxidize less than half of the sulphur in pyrite in the same time. This remaining sulphur was held very tenaciously, though the mineral was subjected to more powerful currents and longer continued action than in the case of marcasite or pyrrhotite. Finally, by adding an equal quantity of CuO , and using a more powerful current, all of the contained sulphur was oxidized. Previous to the addition of CuO but 21 or 23 per cent of the sulphur was oxidized. In concluding the article above referred to the author questions whether the crystalline form alone can make this difference in the action of the two minerals when under the influence of the current.

The two samples of pyrite and marcasite that I selected for the following study were chosen after considerable examination of material as being typical of the two forms of FeS_2 . The pyrite was from the hematite mines of Elba. It is exceptionally pure and free from decomposition or tarnish. Before deciding on it finally pieces were ground and polished and then examined under the microscope with powers ranging from 50 to 200 diameters, in order to see if it contained any enclosures or varied in texture. It was perfectly homogeneous and showed no enclosures. It took a high polish. The crystals showed the combination of octahedron and pentagonal dodecahedron $O + \frac{2}{3}2$. Some of the crystals were coated in places with scales of hematite, but this was all carefully removed in breaking up material for experiment. The color was bright brass-yellow, the specific gravity was determined as 5.179. The marcasite was from the zinc mines of the Subcarboniferous of Joplin, Jasper county, Mo., finely crystallized in polysynthetic twinnings. The freshly broken crystals show a greenish yellow color, almost white, but they tarnish readily with bluish or brownish colors. No gangue was present, everything dissolving completely in nitric acid. This marcasite was examined with the microscope in the same way as the pyrite; it did not take such a high polish on account of a fibrous structure, but no foreign matter was found with a power of 200 diameters. Its color was uniform throughout, showing that no pyrite was present. The specific gravity as determined was 4.844.

In preparing material for experiment only sufficient was ground for im-

**Jour. Franklin Inst.*, Vol. cxxx, pp. 152-154.

mediate use to avoid any chance of oxidation of the ground material ; the stock samples of the two minerals broken to nut size were kept in stoppered bottles. The grinding of material was continued as long as grit appeared, but no bolting was resorted to.

As the experiments of Prof. Smith on oxidation by the electric current showed such remarkable results, my first experiments were on oxidation. As an oxidizing agent potassium permanganate (KMnO_4) was used, several strengths of which were tried for varying intervals of time with each mineral, and the amount of sulphur oxidized to sulphuric acid determined in the liquid by precipitating as barium sulphate. The object was to secure a complete series of results which would show the comparative rates of oxidation of the sulphur in the two minerals. Neutral aqueous solutions of the potassium permanganate were used, and the strengths of solution employed were $\frac{1}{100}$ normal, one per cent., three per cent. and five per cent.; the periods of oxidation extending over one, two, three, four and five hours, and the entire series being performed at ordinary temperatures and at 100° . As duplicate determinations were made in the majority of cases (I made about 130 determinations of sulphur as barium sulphate), this work consumed a large amount of time and prevented as full a study of some other reactions of the two minerals as had been originally intended. The following are the detailed descriptions of my processes and results :

ACTION OF $\frac{1}{100}$ NORMAL POTASSIUM PERMANGANATE SOLUTION AT ORDINARY TEMPERATURE.

These oxidations were performed as follows : Two-tenths of a gram of the finely powdered mineral was placed in a stoppered bottle of about 100 c.c. capacity, then 50 c.c. of the permanganate solution added and the contents of the bottle violently shaken to break up lumps. This shaking was repeated about every fifteen minutes while the oxidation lasted. The temperature of the room was at the same time recorded. As stated, the oxidation was continued for one, two, three, four and five hours with each mineral, making at least ten experiments necessary for each strength of solution. After the solution had acted for the required time it was rapidly filtered through asbestos with aid of the filter pump, the filtrate transferred to a beaker, 20 c.c. of concentrated hydrochloric acid added, and the whole heated until all manganese was reduced to manganous chloride. If not too acid the solution was then diluted to about 300 c.c. and the sulphuric acid precipitated as barium sulphate. When very acid, excess of hydrochloric acid was removed by evaporation or by adding ammonia, the ammonium chloride seeming to facilitate the precipitation. The precipitate was washed with hot water and then weighed. All precipitations were made at boiling temperature and digested hot for at least two hours, and then cold for at least twelve hours more before filtering. The filtrates from most of the cold tests were re-

duced with metallic zinc and titrated with permanganate, but no iron was found in the solution.

The two minerals did not present the same appearance when acted on by the oxidant. Pyrite retained its color and seemed as pulverulent as when the permanganate was added, but marcasite immediately on the addition of the reagent became coated with manganese dioxide, took on a brownish color, and showed a tendency to cake together and stick to the sides of the bottle, so that it was with difficulty dislodged. This tendency of the marcasite was more marked with stronger solutions of the permanganate and was doubtless the cause of much of the irregularity that will be noticed in the results. The reason for this difference in action of the reagent on the two minerals will be discussed later on.

The percentages of sulphur oxidized in the two minerals by this method are shown in the following table, where all results that were obtained are recorded. The figures show the percentages of sulphur oxidized, calculated on the basis of FeS_2 equal to one hundred per cent. It will be noted that the four-hour oxidation of marcasite shows a result that is less than the two-hour. This was due to caking of the mineral against the walls of the bottle, which prevented much of it from coming in contact with the solution. On the whole, this series was about the most satisfactory of the cold experiments with KMnO_4 , the action of this dilute solution being less rapid and hence more even than that of the more concentrated solutions; naturally the action ceases with a certain dilution, and hence the four- and five-hour oxidations of pyrite are about equal.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a $\frac{1}{100}$ N. Solution of KMnO_4 at 22° .

MINERAL.	1-HOUR.	2-HOUR.	3-HOUR.	4-HOUR.	5-HOUR.
Pyrite with $\frac{1}{100}$ N. solution KMnO_4	.78	1.17	1.38	1.74	1.72
Marcasite with $\frac{1}{100}$ N. solution KMnO_4	1.07	1.86	2.04	(1.25)	2.38

The curves formed by plotting these results on rectangular coördinates are shown in Pls. i and ii. They are marked 22° M_1 for the marcasite and 22° P_1 for the pyrite.

ACTION OF 1 PER CENT. POTASSIUM PERMANGANATE SOLUTION AT ORDINARY TEMPERATURE.

This and also the two following series were performed as described under $\frac{1}{100}$ normal solution above. At least two experiments were tried with each mineral in this and the two following cold oxidations, and whenever a result was notably higher or lower than its dupli-

cate a third or fourth was tried. The tendency of the marcasite to cake, noted in the previous series, became still more marked here, and is doubtless the cause of one of the four-hour oxidations (marked by parenthesis) being notably lower than the three-hour. Such a result is obviously incorrect. On the other hand, the result in the three-hour column which is placed in parenthesis is the highest obtained. This experiment was made at the same time as the one showing 1.93 per cent., but the room was very warm (25°), which may in part account for this high result. It will be noticed that the oxidation of the pyrite seems to stop at the three-hour trial, those following showing no appreciable increase. This is well seen in the graphic representation of these oxidations (Pls. i and ii).

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 1 Per Cent. Solution of KMnO_4 at 22° .

MINERAL.	1-HOUR.	2-HOUR.	3-HOUR.	4-HOUR.	5-HOUR.
Pyrite with 1 per cent. solution KMnO_4 cold.	1.72	1.38	1.85	1.79	1.70
	1.71	1.47	1.87	1.90	1.89
Marcasite with 1 per cent. solution KMnO_4 cold.	1.16	1.29	1.93	1.95	2.01
	1.28	1.13	2.19 (3.92)	(1.56) 2.69	2.15 2.55

ACTION OF 3 PER CENT. SOLUTION OF POTASSIUM PERMANGANATE AT ORDINARY TEMPERATURE.

The conditions of this series of experiments were the same as those of the last. The tendency of the results to fluctuate instead of showing a gradual progression is now very marked. One of the one-hour pyrite oxidations shows more sulphur oxidized than is shown by any other individual result of the series. No explanation can be offered for such a discrepancy as this. On the other hand, the high result shown in the three-hour oxidation is quite easily explained by the marcasite having been little, if any, caked in this experiment. The two low results of pyrite three hour and marcasite four-hour oxidations are readily explicable on the ground of caking of the material. As the barium sulphate was often determined several days after the oxidation was completed, it is obvious that no reliable notes could be made concerning the caking or non caking of the mineral in the permanganate. With this strength of solution it is evident, too, that the main action of the permanganate is complete at the end of one hour, notably in the case of the marcasite, and it is only when very vigorous agitation exposes fresh surfaces of the mineral to the action of the KMnO_4 that any further action can take place. We therefore see that marcasite in one hour gives up as much sulphur as in five hours, and this is very graphically shown on Pl. i.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 3 Per Cent. Solution of KMnO_4 at 22° .

MINERAL.	1-HOUR.	2-HOUR.	3-HOUR.	4-HOUR.	5-HOUR.
Pyrite with 3 per cent. solution KMnO_4 cold.	1.65 (3.55)	2.23 2.31	2.80 (1.58)	2.47 2.62	2.81 2.28
Marcasite with 3 per cent. solution KMnO_4 cold.	2.72 2.87	2.17 2.33	2.87 (3.31)	2.88 (1.89)	2.83 2.77

ACTION OF 5 PER CENT. SOLUTION OF POTASSIUM PERMANGANATE AT ORDINARY TEMPERATURE.

In this series, as in the last, the action, as far as pyrite was concerned, was practically complete at the expiration of the first hour, but in the case of the marcasite this point was not reached until probably the end of the second hour, and, in fact, in one case was progressive to the end. But one very great discrepancy is to be noted here in the three-hour column with marcasite. The low result in the next column is explained by caking.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 5 Per Cent. Solution of KMnO_4 at 22° .

MINERAL.	1-HOUR.	2-HOUR.	3-HOUR.	4-HOUR.	5-HOUR.
Pyrite with 5 per cent. solution KMnO_4 cold.	2.39 3.15	3.03 3.15	3.22 2.32	2.89	2.79 3.24
Marcasite with 5 per cent. solution KMnO_4 cold.	2.10 2.52	3.06 3.76	3.82 (5.83) 2.77	3.16 (2.44)	3.39 4.17

This series finishes the experiments at ordinary temperatures. In all of them the action was comparatively slight, not exceeding at most 10 per cent. of the contained sulphur in the mineral which would not be sufficient to show any marked difference between the two minerals as bearing on their constitution, if the constitution which seems to be indicated by subsequent experiments (to be presently described) is the true one.

The oxidations with potassium permanganate at a temperature of 100° were conducted by suspending the vessel containing the mineral and solution in boiling water. Both stoppered bottles and thin glass flasks closed with perforated corks were used for this series of experiments. The water was kept continually boiling and the bottles or flasks were immersed deep enough to cover that portion of them containing the permanganate. Six or eight oxidations were made at one operation. The

permanganate solution, after it had acted the required time, was treated as in the experiments conducted at ordinary temperatures described above. Much more active oxidation took place at this temperature (100°), but the tendency of the mineral to cake together was much more marked, and now this took place with pyrite as well as with marcasite. Moreover, the deposition of manganese dioxide in every case was now very great, causing often a stoppage of the oxidation until it could be dislodged. As these oxidation experiments had already occupied much time only one trial was now made at each concentration of solution for each hour from one to five, unless, as before, marked discrepancies occurred, when two or more trials were made. The series of results are hence not so regular as they would have been had more trials been made, these irregularities arising from the difficulties that have been mentioned, as well as from the fact that the dilute solutions soon became exhausted, and that all solutions suffered some evaporation, but some more than others, causing irregular strength with the same solution. Nevertheless, the results agree in kind with those obtained at ordinary temperature, but differ widely in degree. Whereas at ordinary temperature the greatest amount of sulphur oxidized in marcasite by the five-hour trial with 5 per cent. permanganate was 4.17 per cent., at 100° this became 16.36 per cent, or about four times as much.

ACTION OF $\frac{1}{100}$ NORMAL POTASSIUM PERMANGANATE SOLUTION AT 100° .

The results given in the following table show perhaps more strongly than either of the other series of experiments at 100° the effect of the different disturbing causes that have been mentioned. It especially shows the effect of caking of the pyrite, which now came in as an important disturbing factor. The result of this caking is shown in the three- and four-hour results with pyrite, both being very low. Marcasite, on the other hand, invariably caked and stuck to the bottom of the bottle, but as this was a constant source of error in this case, the results show a gradual and fairly even increase. Irregular results with marcasite were now largely conditioned by the evaporation of the solution or by the fact of whether the mineral was evenly caked over the inner surface of the vessel or concentrated in spots. The result of this latter way of caking will be better seen in some of the subsequent series of experiments.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a $\frac{1}{100}$ Normal Solution of $KMnO_4$ at $100^{\circ} C$.

MINERAL.	1-HOUR.	2-HOUR.	3-HOUR.	4-HOUR.	5-HOUR.
Pyrite with $\frac{1}{100}$ N. $KMnO_4$ at $100^{\circ} C$	4.05	4.72	3.36	2.04	5.64
Marcasite with $\frac{1}{100}$ N. $KMnO_4$ at $100^{\circ} C$	3.17	3.84	3.76	5.63	5.61

ACTION OF 1 PER CENT. POTASSIUM PERMANGANATE SOLUTION AT 100°..

The results of the oxidation shown in this series are chiefly remarkable as still further illustrating the action of the solution on the caked material, as shown in the four- and five-hour trials with pyrite and the four-hour trial with marcasite. This latter shows, too, the effect of having* the caked mineral massed in one spot. With this exception, the marcasite oxidations are progressive and fairly uniform (the two hour trial falls somewhat below what it doubtless should be), but the pyrite shows a sharp fall in the four- and five-hour trials. The cause of this has been indicated. That the concentration of the solution by evaporation caused an increase in the action seems to be indicated by the result of the five-hour marcasite oxidation, but this is much more strongly marked in the 5 per cent. series in the case of pyrite, which will be referred to later on.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 1 Per Cent. Solution of $KMnO_4$ at 100°.

MINERAL.	1-HOUR.	2-HOUR.	3-HOUR.	4-HOUR.	5-HOUR.
Pyrite with 1 per cent. $KMnO_4$ at 100° C.	6.03	6.98	8.33	6.11	6.88
Marcasite with 1 per cent. $KMnO_4$ at 100° C.	6.43	5.61 6.25	8.56	7.40	9.10

ACTION OF 3 PER CENT. SOLUTION OF POTASSIUM PERMANGANATE AT 100° C.

The average results of this series of oxidations were very good, with the exception of two members of the series—the marcasite five-hour trial and the pyrite three-hour. This latter was repeated, but with a similar low result. Leaving these two out of account, the average results show a very fairly even rate of progression, which have been brought out in the diagram (Pl. i). It is evident from an inspection of the following table that the marcasite oxidations of the four- and five-hour trials were arrested by some disturbing influence.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 3 Per Cent. Solution of $KMnO_4$ at 100° C.

MINERAL.	1-HOUR.	2-HOUR.	3-HOUR.	4-HOUR.	5-HOUR.
Pyrite with 3 per cent. $KMnO_4$ at 100° C.	5.53 (7.01)	5.77 7.89	6.81 5.16	10.73	11.08
Marcasite with 3 per cent. $KMnO_4$ at 100° C.	5.25 5.50 (8.67)	7.97	9.42	9.80	7.55

ACTION OF A 5 PER CENT. POTASSIUM PERMANGANATE SOLUTION
AT 100° C.

This series was decidedly the most satisfactory of the experiments conducted at 100° and, with the exception of the two-hour oxidations, in case of each mineral shows a remarkably regular increase in the oxidation of the sulphur. It illustrates, too, in the case of the pyrite, the effect of the concentration of the solution due to evaporation. This causes a more rapid rise in the results after three hours' action, and notably between four and five hours. This rise is not so well seen from the table as from the plot of the results given in Pl. i. Here this rising of the curve after three hours is very marked as contrasted with the curve of the marcasite oxidations.

*Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite
by a 5 Per Cent. Solution of $KMnO_4$ 100°.*

MINERAL.	1-HOUR.	2-HOUR.	3-HOUR.	4-HOUR.	5-HOUR.
Pyrite with 5 per cent. $KMnO_4$ at 100° C.....	7.95	7.52	9.85	11.86	14.98
Marcasite with 5 per cent. $KMnO_4$ at 100° C.....	8.38	8.38	13.27	14.85	16.36

The graphic representation of the rate of oxidation of sulphur in these two minerals is plotted from the following tables, the first of which shows the average amounts of oxidation of sulphur compiled from the several small tables already given. In this compilation I have omitted a few of the results given in parentheses in the small tables as they are evidently incorrect, and would vitiate the averages. On the other hand, I have simply retained the parentheses of the small tables in certain cases where but one result was obtained. The second table, also compiled from the several small tables, shows for the experiments at ordinary temperature the result of selecting, wherever possible, such individual determinations as show a progressive increase in the oxidation. In this way more regular series of results are obtained. Inasmuch as the variations are so marked, this method of selecting results seems justified, at least for obtaining a comparison of the relative rates of oxidation of the sulphur in the two minerals. The results of Table i are plotted in Pl. i, and those of Table ii in Pl. ii.

I. Table Showing Average Relative Oxidation of Sulphur in Pyrite and Marcasite by Solutions of $KMnO_4$ at 22° and at 100° . See Pl. i.

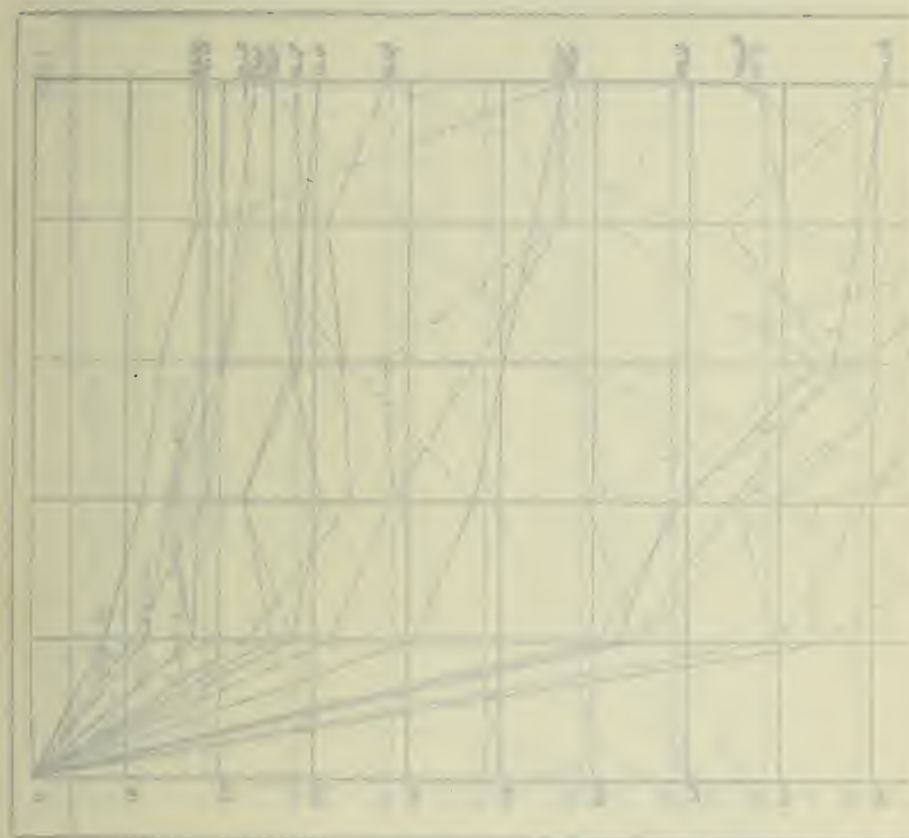
MINERAL.	1-HOUR	2-HOUR	3-HOUR	4-HOUR	5-HOUR	ON PL.
Pyrite $\frac{1}{100}$ N. cold	.78	1.17	1.38	1.74	1.72	$22^\circ P_1$
Marcasite $\frac{1}{100}$ N. cold	1.07	1.86	2.04	(1.25)	2.38	$22^\circ M_1$
Pyrite 1 per cent. cold	1.71	(1.43)	1.86	1.85	1.80	$22^\circ P_2$
Marcasite 1 per cent. cold....	1.22	1.21	2.06*	2.32*	2.24	$22^\circ M_2$
Pyrite 3 per cent. cold	2.55	2.27	2.80*	2.55	2.55	$22^\circ P_3$
Marcasite 3 per cent. cold....	2.80	2.25	2.87*	2.88*	2.80	$22^\circ M_3$
Pyrite 5 per cent. cold	2.77	3.09	2.77	2.89	3.02	$22^\circ P_4$
Marcasite 5 per cent. cold....	2.31	3.41	3.30*	3.16	3.78	$22^\circ M_4$
Pyrite $\frac{1}{100}$ N. 100°	4.05	4.72	3.36	2.04	5.64	$100^\circ P_1$
Marcasite $\frac{1}{100}$ N. 100°	3.17	3.84	3.76	5.63	5.61	$100^\circ M_1$
Pyrite 1 per cent. 100°	6.03	6.98	8.38	6.11	6.88	$100^\circ P_2$
Marcasite 1 per cent. 100°	6.43	5.93	8.56	7.40	9.10	$100^\circ M_2$
Pyrite 3 per cent. 100°	6.26	6.83	6.81*	10.73	11.08	$100^\circ P_3$
Marcasite 3 per cent. 100°	6.47	7.97	9.42	9.80	(7.55)	$100^\circ M_3$
Pyrite 5 per cent. 100°	7.95	7.52	9.85	11.86	14.98	$100^\circ P_4$
Marcasite 5 per cent. 100°	8.38	8.38	13.27	14.85	16.36	$100^\circ M_4$

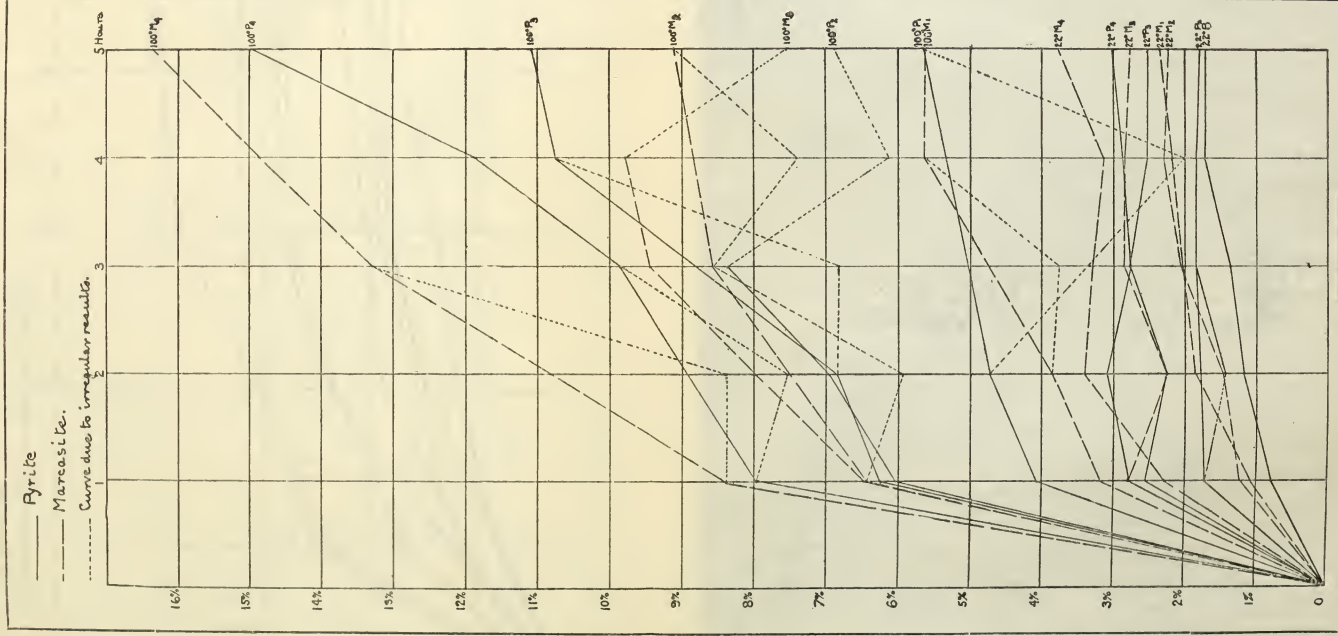
II. Table Showing Selected Results of the Oxidation of Sulphur in Pyrite and Marcasite by Solutions of $KMnO_4$ at 22° . See Pl. ii.

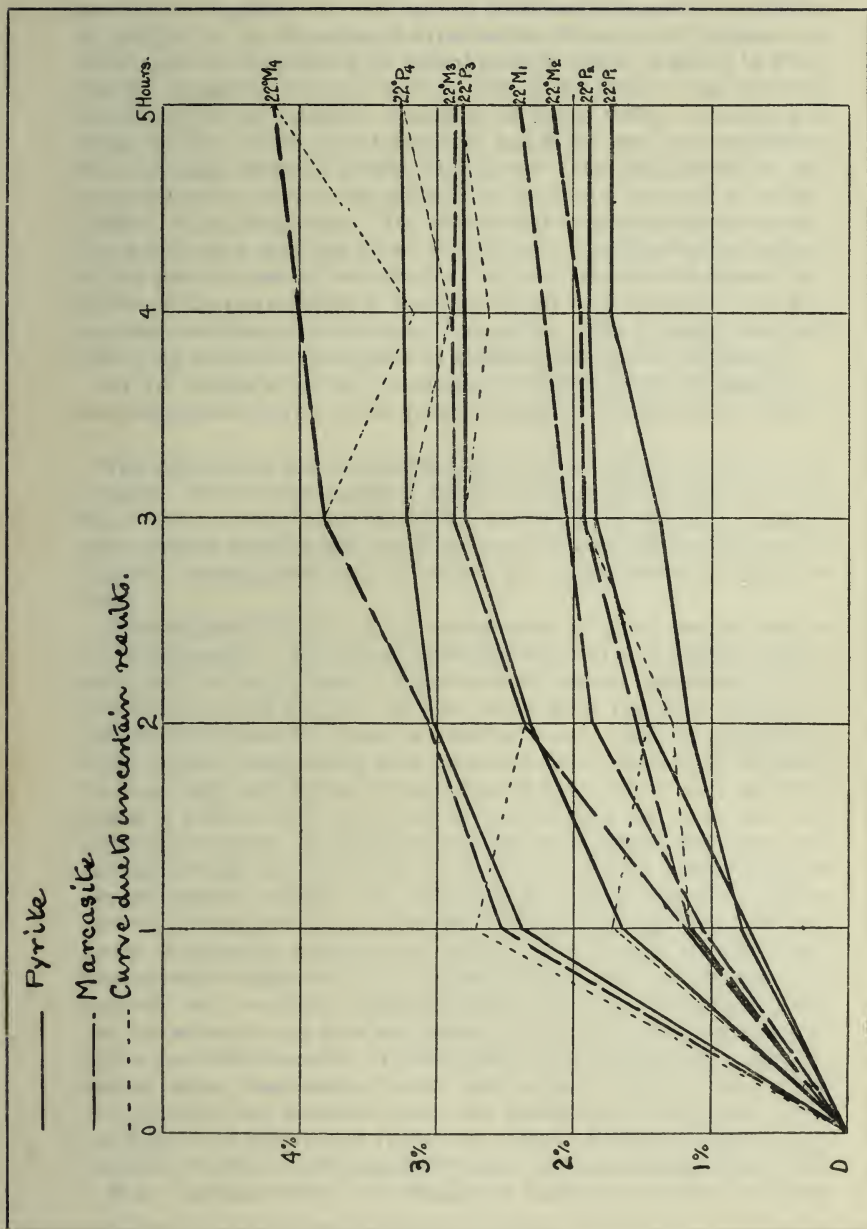
MINERAL.	1-HOUR	2-HOUR	3-HOUR	4-HOUR	5-HOUR	ON PL.
Pyrite $\frac{1}{100}$ N. cold	.78	1.17	1.38	1.74	(1.72)	$22^\circ P_1$
Marcasite $\frac{1}{100}$ N. cold	1.07	1.86	2.04	(1.25)	2.38	$22^\circ M_1$
Pyrite 1 per cent. cold	(1.71)	1.47	1.85	1.90	1.89	$22^\circ P_2$
Marcasite 1 per cent. cold....	1.16	1.29	1.93	1.95	2.15	$22^\circ M_2$
Pyrite 3 per cent. cold	(1.65)	2.31	2.80	(2.62)	2.81	$22^\circ P_3$
Marcasite 3 per cent. cold....	(2.72)	2.33	2.87	2.88	2.83	$22^\circ M_3$
Pyrite 5 per cent. cold	2.39	3.03	3.22	(2.89)	3.24	$22^\circ P_4$
Marcasite 5 per cent. cold....	2.52	3.06	3.82	(3.16)	4.17	$22^\circ M_4$

In plotting from these tables a vertical scale of one-half inch per one per cent. of sulphur oxidized and a horizontal scale of three-quarters inch per hour of oxidation have been employed. Wherever there was a drop in the results the gap has been bridged over by the main curve, thus making the curves as nearly as possible progressive, but the drop has been plotted in fine dotted lines. On examining these curves the points as to the relative rates of oxidation that have been mentioned are shown very graphically, the curve of the marcasite oxidation rising in each case above the corresponding one of pyrite, but both showing a similar form. Of these curves the $\frac{1}{100}$ normal solution cold and the 5 per cent. solution hot

* Obtained by omitting discordant results.







are the most regular. No very marked difference in the rate of oxidation is brought out by this series of experiments, the amount of sulphur oxidized never having reached the critical point in pyrite, as shown by Prof. Smith's oxidations with the current already described. This point at which the rate of oxidation of sulphur in pyrite suffers a change was found by Prof. Smith to be between 21 and 22 per cent. from the results of a very large series of current oxidations.* The explanation for this being the critical point in the oxidation of pyrite will be given in the discussion of its constitution. The experiments with permanganate oxidation simply show then that up to near this point (the highest point reached in the pyrite oxidation was nearly 15 per cent.) the relative rates of oxidation of the two minerals do not differ widely from each other, but that marcasite oxidizes somewhat faster than pyrite. This is simply what has been long known and recognized in regard to atmospheric weathering.

As will be seen when the constitution of these minerals is considered, marcasite cannot have a critical point in regard to oxidation of its sulphur.

The experiments thus far described had for their object the removal of sulphur. On the other hand, a number of ways of attacking the iron were tried and with more interesting results. In these trials reagents were selected which would attack the iron more energetically than the sulphur. Among these may be classed the experiments of solubility in acids.

Hydrochloric acid (hot or cold, concentrated or dilute) has little action on these minerals. Pyrite was treated for one hour with boiling concentrated HCl, of specific gravity 1.20 in covered beakers, and showed in the solution only 2.56 per cent. of iron out of 46.67 per cent. Marcasite, treated in the same way, gave an identical result. Similar experiments at the ordinary temperature were tried with both minerals, by digesting for three days with excess of concentrated hydrochloric acid and with excess of $2\text{HCl} + 3\text{H}_2\text{O}$, but even after three days the action was very slight in both cases. Pyrite gave with both concentrated and dilute acid the same result—a solution of 1.51 per cent. of iron. Marcasite gave almost identical results. The concentrated hydrochloric acid solution showed 1.51 per cent. of iron, the dilute solution 1.89 per cent. No evolution of hydrogen sulphide was detected by lead paper in either case. Concentrated sulphuric acid at boiling temperature decomposes both minerals, with evolution of sulphur dioxide and the separation of sulphur, but the action is very slow and seems to take place more readily with pyrite than with marcasite. Pyrite digested with concentrated sulphuric acid at boiling temperature for one hour showed 14.81 per cent. of the iron dissolved, but marcasite under like conditions was only attacked in one hour to the extent of 12.77 per cent. of iron. Trials were also made in the cold, but did not differ materially from the results obtained with HCl.

More important results were obtained by conducting dried hydrochloric

* Private communication from Prof. E. F. Smith, 1893.

acid gas over the minerals at an elevated temperature. In these trials, 0.2 gram of the mineral was placed in a porcelain boat and heated in a glass tube in a strong stream of the gas. The sulphur in the series of experiments at the lower temperature was collected by passing the gas through bulbs containing $\text{Br} + \text{HCl}$; at the higher temperatures, the residue in the boat was analyzed and the sulphur lost estimated by difference. In the experiments at low temperature the entire tube was exposed to a temperature of 210° , as determined by thermometer. The HCl was passed over in a strong stream for one hour. The action at this temperature was slight; the results obtained do not, however, show the entire amount of sulphur removed, as some remained in the cool end of the tube, from the dissociation of the hydrogen sulphide. As the action was so slight, no attempt was made to collect and estimate this sulphur remaining in the tube. In the bromine and hydrochloric acid solution was found sulphur as follows :

Pyrite at 210° in current of HCl (a).....	0.94
“ “ “ “ (b).....	0.93
Marcasite at 210° in current of HCl (a).....	0.77
“ “ “ “ (b).....	0.59

More marked results were obtained by increasing the temperature. Similarly conducted experiments were carried out at 310° and 325° , the time of heating ranging from one to three and one-half hours. The temperature of 310° was graded by keeping it between the melting points of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (300°) and NaNO_3 (313°), the higher temperature was between the last 313° and the melting point of KClO_3 (334°). After the HCl had been passed for a sufficient length of time, the tube was allowed to cool (with the gas current continued until cold) and then the remaining sulphur estimated by oxidizing the contents of the boat with nitric acid and potassium chlorate and precipitating and weighing as BaSO_4 . The amount found, subtracted from 53.33 %, gave the loss of sulphur. In this case the results obtained by oxidation were reversed, the pyrite lost more sulphur than the marcasite. This is an expression of the fact that the hydrochloric acid gas (or its contained Cl) acts more vigorously on the iron of pyrite than on that of marcasite. The results of the reaction were in each case ferrous chloride in the boat and free sulphur in the tube, the latter from dissociation of the hydrogen sulphide. No ferric chloride was seen in the tube, except a trace with the pyrite. Each mineral was heated for one hour at 310° in a current of the gas and showed loss of sulphur as follows :

Pyrite heated at 310° for 1 hour in HCl , sulphur lost.....	10.73
Marcasite “ “ “ “ “	7.19

About the same relative amounts were lost on heating for three and one-half hours at 325° . The results thus obtained were as follows :

Pyrite heated at 325° for $3\frac{1}{2}$ hours in HCl , sulphur lost....	17.13
Marcasite “ “ “ “ “	10.70

Besides these two experiments, pyrite was heated for one hour at a red heat in a stream of the gas. A copious sublimate of ferrous chloride was found in the tube, with a trace of ferric chloride and sulphur. This time the loss was 46.47 per cent. of sulphur. It seems evident from these experiments that, as above stated, the iron in pyrite is in a condition that is more readily acted on by hydrochloric acid than is the iron in marcasite. It will be proved that the iron in marcasite is all ferrous, while part of that in pyrite is ferric, and this is probably the explanation of the above phenomenon. All of the iron in each case described above would form ferrous chloride (FeCl_2) on account of the reducing action of the hydrogen sulphide formed. Under the conditions of the above experiments, the critical point developed in the oxidation of pyrite was not reached, but it is not likely that it exists with this reagent, or if there be a critical point it is not 21 per cent. The thought suggested itself to me that perhaps some sulphur would be lost in pyrite if it were heated to 325° in a neutral atmosphere, and that this might account for the difference shown in the loss of sulphur in the two minerals. This proved not to be the case. Pyrite heated in this way in an atmosphere of nitrogen gave no appreciable loss after one hour at a temperature of 325° .

Instead of hydrochloric acid gas, the action was tried of ammonium chloride at temperatures up to 335° and in an atmosphere of nitrogen. Under these conditions the sulphur was combined as ammonium sulphide probably and did not exert such a reducing action on the iron. These experiments were conducted as follows: 0.2 gram of the finely pulverized mineral was mixed with 0.5 gram dry ammonium chloride and introduced (in a porcelain boat) into a glass tube. Test samples of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ and KClO_3 in sealed tubes were used to regulate the temperature. All air was displaced in the tube by nitrogen and a slow current of nitrogen passed through the tube before heating. Under these conditions with marcasite, sulphur and ammonium sulphide were found sublimed in the tube along with ammonium chloride, and in the boat there was found much ferrous chloride without any ferric chloride, but in the case of the pyrite there was formed a large proportion of ferric chloride, which sublimed on the tube towards the end of the operation. The heating was conducted slowly in each case and continued until all ammonium chloride was sublimed from the boat, the temperature of 335° not being exceeded during this time. The entire operation lasted about twenty-five minutes in each case. Three trials of each mineral were made and with the same result in each case; with marcasite only ferrous chloride was found in the boat and no iron in the tube, pyrite always gave much ferric chloride and little ferrous. The amounts of sulphur removed are probably not very significant; they showed the following results:

Pyrite heated with NH_4Cl lost sulphur (a).....	7.03
“ “ “ “ (b).....	7.10
Marcasite “ “ “ (a).....	9.50

The important point brought out in these experiments is that pyrite contains a large amount of ferric iron, while in marcasite the iron apparently exists in the ferrous condition. Some reducing action might, however, have taken place, due to the sulphides formed. The condition of the iron in the chlorides found in the boat and tube was very carefully tested by several reagents in each case, and there can be no doubt as to the correctness of the results as stated above.

The decomposition of the sulphides by metallic salts seemed to offer some hope of being productive of results that would show in a quantitative way the exact amounts of ferrous or ferric iron that are present in these two minerals. In this line, the action of gold chloride, silver nitrate and silver sulphate were tried in a qualitative way with both minerals. Of these, the first gave a ready decomposition with both, and produced both ferrous and ferric salts in each case. The silver nitrate gave a similar result. Silver sulphate acted very slowly and without any definite results.

The action of copper sulphate in neutral solution and under pressure was tried with very remarkable results. At the ordinary temperature and pressure the solution of this salt has little effect on either mineral, and the same is true of the solution at a boiling temperature, but under pressure the reaction is complete. The experiment was conducted as follows: 0.2 gram of the finely pulverized mineral was introduced into a stout glass tube, and 50 c.c. of a 10 per cent. solution of the salt, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, added, the air displaced with a pinch of NaCO_3 and a drop or two of H_2SO_4 (dilute), and a heavy seal made on the tube. The tubes containing the two minerals were heated for six hours in an autoclave to a temperature of about 200°C . The contents of the tubes were found to contain no traces of undecomposed mineral, but there was a black, more or less flocculent precipitate in its place. This proved to be copper sulphide. The solution had not altered appreciably in appearance. The liquid contents of the tube were in each case transferred to a flask previously filled with CO_2 and with 10 c.c. dilute sulphuric acid in the bottom, the tube then rinsed with water and the amount of ferrous iron present titrated with freshly standardized potassium permanganate. In the case of marcasite this gave 18 c.c. KMnO_4 solution (this was two- or three-tenths of a cubic centimeter too much, on account of the difficulty in catching the end reaction). To correct this for the iron in the copper sulphate, a blank of 50 c.c. CuSO_4 solution, the same as used above with 10 c.c. dilute sulphuric acid, was titrated with the permanganate, giving 0.5 c.c. reduction. The factor of the permanganate was .0054 gm. Fe for 1 c.c. Making the correction for the reduction of 50 c.c. CuSO_4 solution, this gives 47.25 per cent. of iron in solution as against 46.67, the theoretical amount in FeS_2 . No doubt if the end reaction had been more exact there would have been a still closer correspondence in the result.

The tube containing the pyrite was treated in exactly the same manner, and gave a reduction of permanganate of 3.8 c.c. This time the end

reaction was sharp and exact. Calculating the above to iron (after making correction for CuSO_4) this gives 8.91 per cent. of ferrous iron in pyrite. As the total iron is 46.67, this corresponds to 19.09 per cent. of the iron in the mineral, or almost exactly one-fifth. These experiments demonstrate in a positive manner the condition of the iron in the two minerals, and even show the exact amounts of each condition of the iron, ferrous and ferric.*

That marcasite should hence be more readily decomposed by oxidation than pyrite seems fully explained by the foregoing investigations, as it consists of $\text{Fe}''\text{S}_2$, an unsaturated compound. In this compound, sulphur must link to sulphur, or the compound have unsaturated bonds, and hence any element which would attack the sulphur would break up the compound. On the other hand, the iron is held to the sulphur by its full number of bonds, and any substance that has an affinity for iron could not so readily attack it in this condition. This would be true whether ferrous iron be considered here as Fe_2 , with a valence of four, or as Fe'' . That marcasite is $\text{Fe}''\text{S}_2$ is also indicated by its oxidation in the air into FeSO_4 mainly. Under these same conditions it will be noted that pyrite forms both ferrous and ferric compounds, as FeSO_4 , but much more $\text{Fe}_4\text{O}_3(\text{OH})_6$ and free sulphur. Marcasite, however, when decomposed by water under pressure (in nature) forms much limonite also, this being due no doubt to the oxidation being effected under pressure. This constitution explains also the fact that the oxidation of marcasite is continuous and complete, as shown by the current oxidations. It will be shown also that this constitution of pyrite that has been made out explains fully its action with the current. That marcasite is unsaturated is also indicated by the fact that it has not been made artificially or at any rate positively identified in any of the artificial FeS_2 that has thus far been made. If marcasite be a persulphide, as its formula would seem to indicate for a ferrous compound, none of the methods detailed above for making FeS_2 would be applicable in its case, unless perhaps the method of Deville might produce it. All of the other methods would probably produce ferric iron, at least in large part, and the resulting product would be pyrite.

The formula for pyrite derived from my investigations and expressing the relation of the two conditions of the iron in the simplest way is $4\text{Fe}^{\text{iv}}\text{S}_2 \cdot \text{Fe}''\text{S}_2$. This formula is also borne out by what we know of the formation of pyrite as given in the early part of this paper, and by such experiments as I have made on its decomposition, as well as the fact above alluded to that it, in oxidizing in nature, does not form much ferrous compounds but mainly ferric. And it also explains the fact that it is more stable as regards any element attacking its sulphur, for it is most probable that all the sulphur of the $\text{Fe}''\text{S}_2$ in its formula is linked to iron. I would propose the following structural formula, not as expressing the exact constitution of the compound, for of that we know nothing, but as an

* These results have been confirmed by experiments made during the past year in this laboratory, and not yet published.

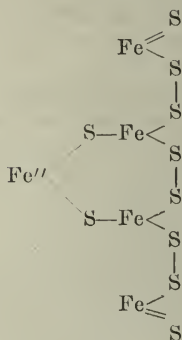


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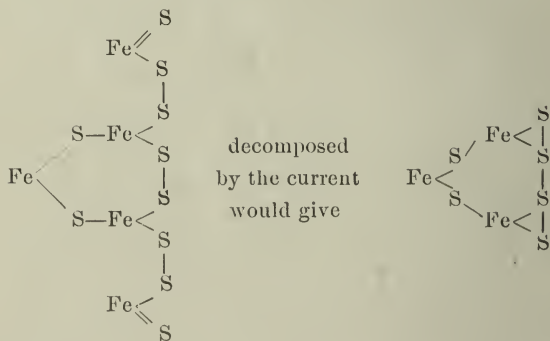
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expression of the condition of the iron in the molecule and as embodying in a quantitative way the result of my investigations into its constitution. It will be noticed that the sulphur of the $\text{Fe}''\text{S}_2$ is made to link entirely with iron.

Structural formula of pyrite.



If ferric iron be considered as $\text{Fe}^{\text{iv}}-\text{Fe}^{\text{iv}}$ it is only necessary to connect the ferric Fe atoms with bonds, but it seems to me that ferric iron is more likely Fe''' , and at any rate this is the simplest way to regard it. A very striking proof of the correctness of the idea expressed in this structural formula that $\text{Fe}''\text{S}_2$ in pyrite has its sulphur all linked to iron is afforded in the experiments on oxidation of the mineral by means of the electric current as detailed above. It will be recalled that the amount thus oxidized was between 21 and 22 per cent. Now if two molecules of FeS_2 be split off from the above formula, say those linked by sulphur to sulphur there would remain a saturated compound much more difficult to decompose (theoretically) than the pyrite molecule illustrated and the amount of sulphur thus removed would be by calculation 21.33 per cent. This action could be thus illustrated :



Of course this structural formula is only intended to represent the